

Final Report to NASA

"Containerless Processing of Undercooled Melts"

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## Abstract

The investigation has focused on the control of microstructural evolution in Mn-Al, Fe-Ni, Ni-V, and Au-Pb-Sb alloys through the high undercooling levels provided by containerless processing, and has provided fundamental new information on the control of nucleation. Solidification analysis has been conducted by means of thermal analysis, x-ray diffraction, and metallographic characterization on samples processed in a laboratory scale drop tube system. The Mn-Al alloy system offers a useful model system with the capability of phase separation on an individual particle basis, thus permitting a more complete understanding of the operative kinetics and the key containerless processing variables. This system has provided the opportunity of analyzing the nucleation rate as a function of processing conditions and has allowed for the quantitative assessment of the relevant processing parameters. These factors are essential in the development of a containerless processing model which has a predictive capability. Similarly, Ni-V is a model system that has been used to study duplex partitionless solidification, which is a novel structure possible only in high undercooling solidification processes. Nucleation kinetics for the competing bcc and fcc phases were studied to determine how this structure can develop and the conditions under which it may occur. The Fe-Ni alloy system has been studied to identify microstructural transitions with controlled variations in sample size and composition during containerless solidification. This work has been forwarded to develop a microstructure map which delineates regimes of structural evolution and provides a unified analysis of experimental observations. The Au-Pb-Sb system has been investigated to characterize the thermodynamic properties of the undercooled liquid phase and to characterize the glass transition under a variety of processing conditions. By analyzing key containerless processing parameters in a ground based drop tube study, a carefully designed flight experiment may be planned to utilize the extended duration microgravity conditions of orbiting spacecraft.

## Introduction

The microgravity environment offers new opportunities for the control of solidification processes. Microgravity conditions significantly reduce convection effects allowing for more precise control of melt temperature and composition. Other forces such as sedimentation and hydrostatic pressure are similarly reduced, while the use of acoustic, electromagnetic, or electrostatic fields for sample positioning avoids crucible-induced contamination and nucleation in undercooled reactive melts. Under these unique conditions, microgravity solidification of liquid metal droplets offers an opportunity to produce novel structures which cannot be produced in a terrestrial environment.

Containerless processing in ground-based drop tubes may be used to simulate the microgravity conditions in space via solidification of liquid droplets under free fall conditions. The results of the ground based drop tube study can then be used to identify critical variables in microgravity processing, and the analysis may be used to design and predict the science requirements for space experiments.

The containerless solidification processing of materials in space requires an understanding of the critical variables affecting solidification. Perhaps the most fundamental parameter in solidification processing is the level of melt undercooling prior to solidification. The undercooling level is directly related to the solidification structure, which includes the product phase or phases formed, as well as microstructural morphology and level of refinement. Usually crystallization in bulk liquids is initiated at an unknown heterogeneous nucleation site at a low undercooling level. But when liquids are dispersed into fine droplets, a partitioning of nucleants occurs, allowing for a high undercooling in the nucleant-free fraction of the droplet population. The solidification of a highly undercooled liquid is similar to that produced by rapid liquid quenching, but offers a greater control of nucleation conditions. Previous studies have allowed for the identification of important process variables in optimizing the extent of observable undercooling, and have identified some novel microstructures and microstructural

transitions. In this study the alloy selection has also been based on criteria (i.e., metastable phase diagrams) that can be useful in identifying novel phase selection and microstructure morphologies.

The program has been directed toward the investigation of drop tube and other containerless processing methods in a ground based effort in preparation for a space experiment has focused on the control of novel solidification microstructural development in selected alloys of manganese, nickel, and Au-Pb-Sb.

Containerless processing removes a major source of impurities and heterogeneous nucleation sites, allowing for a large melt undercooling. On earth, containerless processing may be accomplished through levitation melting, or by solidifying molten droplets during free fall. Although these techniques are limited in terms of processing control and to the duration of the microgravity condition, critical variables and their effect on solidification structure may be identified for the planning of containerless processing in space.

Of all the factors influencing solidification structure, perhaps one of the most difficult to control in many processes has been the undercooling level. For example, grain refinement of aluminum castings and inoculation of ductile iron involve processing techniques which are not well understood and are somewhat difficult to control effectively. The study of melts processed in a containerless environment simplifies the analysis of solidification by means of nucleant isolation through droplet dispersal. By studying the solidification behavior in a droplet dispersion, effective nucleation sites may be isolated and identified, allowing for improvement in inoculation techniques and microstructural control.

## **Background**

All practical solidification processes involve some level of melt undercooling. The realization of appreciable levels of liquid undercooling requires some control over the

kinetics of crystal nucleation. A wide variety of catalytic sites for the initiation of crystallization is possible so that the removal of the melt containment vessel as a site can be effective in promoting large undercooling and in studying other potential nucleants.

Containerless processing also allows for physical property measurements that are not accessible by usual techniques. But perhaps the most significant potential for microgravity processing of containerless melts lies in the structural control that is possible. With controlled undercooling supersaturated solid solutions, metastable crystalline phases, novel microstructures, and metallic glass formation are possible as solidification products. In addition, the rapid growth rates associated with large undercoolings often result in a refined microstructural scale and improved mechanical properties.

During solidification at high rates, the nucleation and/or growth of a thermodynamically stable phase from the liquid may be difficult. As a result, the understanding of novel microstructures associated with non-equilibrium phases requires a consideration of the level of undercooling at the onset of nucleation as well as the rapid growth kinetics. Since the available free energy for non-equilibrium phase formation is directly related to the amount of undercooling, increasing levels of undercooling result in an expanded range of possible solidification structures.

The establishment of melt undercooling as a key variable in microstructure development provides an important link between rapid quenching studies and undercooling research. In many respects, undercooling is a more fundamental parameter than cooling rate. In most work on rapid solidification, cooling rate is used as a process variable mainly due to convenience, but in solidification studies on droplet samples [80PERa, 82PER] results have demonstrated that undercooling can be treated in a meaningful way as a process variable. Moreover, the results from droplet experiments have allowed for the identification of possible solidification reaction pathways and the critical variables controlling melt undercooling [82PER, 80PERb]. With this information,

it has been possible to obtain an understanding of containerless processing solidification results.

In the program, the sample processing capabilities of drop tube facilities have provided a controlled containerless environment for studying melt undercooling and solidification structure development. With containerless solidification under free fall conditions, liquid metals are restricted in size since only a limited time is available during which solidification must occur. However, this approach does allow for the identification and control of the key processing parameters that govern the undercooling response. Furthermore, the spectrum of microstructural evolution that is associated with the undercooling response can be established and related to containerless processing variables.

### **Processing Variables of Undercooled Liquid Droplets**

Containerless drop tube processing studies are an important component in the development of an experimental data base for space based microgravity processing of undercooled containerless melts. The initial studies of containerless processing have demonstrated that the droplet studies have a direct relevance to the experience in the undercooling of liquid metals. Therefore, background information (figure 1) on the control of liquid undercooling is useful not only in terms of the interpretation of the initial containerless processing results, but also in understanding the implications of the research program on both terrestrial experiments and future space experiments.

The current research on containerless processing has focused on the phase selection involved in metastable phase formation, the evolution of solidification microstructure, and other aspects of the solidification of undercooled alloys. The experimental approach used to conduct these studies has involved a drop tube system. Experimental results have established that samples may be produced which exhibit large undercoolings prior to solidification during a free fall period of less than one second.

The main objective of the research project was the control of solidification microstructures in manganese and nickel alloys during containerless drop tube processing. Based on previous experience, several processing variables such as particle size, melt superheat, and sample environment have been identified for the control of containerless solidification of droplet samples. Solidification behavior of the droplets was evaluated through metallography, thermal analysis, and x-ray diffraction in conjunction with a heat flow model of processing conditions. The research undertaken has contributed not only new insight and understanding towards terrestrial solidification processing, but has also demonstrated that microgravity materials processing can yield novel microstructures and phases that have not been observed previously with more conventional terrestrial processing approaches.

### **Ni-V Alloy System - Duplex Partitionless Solidification**

[Refer to attachment A1]

High undercooling levels may result in the formation of metastable crystalline structures and amorphous phases, and the rapid solidification rates associated with high undercooling levels may also lead to solute trapping, resulting in the formation of a supersaturated phase. Increasing undercooling below the alloy liquidus expands the range of possible solid compositions which may form from the liquid. When the liquid phase of a given alloy composition is undercooled below a temperature known as  $T_0$ , at which the free energies of the solid and liquid are equal, complete solid trapping may occur, i.e., no segregation develops. This form of freezing is known as partitionless solidification. Partitionless solidification is analogous to massive transformations in solid state reactions. The locus of the  $T_0$  temperatures as a function of alloy composition is known as a  $T_0$  curve, with each solid phase having an associated  $T_0$  curve with respect to the liquid phase. In order for partitionless solidification of a phase to occur, the liquid must be

undercooled below the  $T_0$  temperature for that phase. If the liquid is undercooled below the  $T_0$  temperatures for two different solid phases, a duplex partitionless structure may develop. Duplex partitionless solidification in a binary alloy may be considered the limiting case of a binary eutectic reaction in which the two solid phases have the same composition as that of the liquid. The controlled solid state annealing of such a duplex supersaturated mixture could yield an intriguing dual precipitation pattern of high density dispersions.

To produce the processing conditions necessary to form this structure, the  $T_0$  curves were used as a guide for the selection of an appropriate alloy system and composition. The Ni-V alloy system was selected for this investigation as a model system, based on preliminary work conducted by Ruhl and Giessen [67RUH] and Gudzenko [67GUD] in which alloys near the eutectic composition were found to contain metastable supersaturated fcc and bcc solid solutions following splat quenching. As a guide for alloy composition determination, a regular solution model was used to calculate the metastable Ni-V phase diagram with the lattice stabilities provided by Saunders [88SAU]. High undercooling solidification of Ni-V alloys in this laboratory has resulted in supersaturated fcc and bcc phases over the composition range 47-52 at% V. Extrapolation of lattice parameter vs. composition data for the fcc and bcc phases has revealed that the each solid phase formed from the same composition as that of the bulk liquid for both phases, indicating that a duplex partitionless structure formed during solidification. TEM analysis showed two cellular morphologies in the splat-quenched samples due to a breakdown of plane front solidification. The results of the TEM analysis were very similar to those obtained by Bendersky in the study of partitionless solidification in Ag-Cu alloys [85BEN]. The program has focused on the study of the Ni-V system with containerless drop tube processing as a model system to study duplex partitionless solidification. Due to the reactive nature of vanadium, processing in gas mixtures such as He-H<sub>2</sub> and He-N<sub>2</sub> was conducted to determine the effect of surface coating on the solidification products.

The observation of the duplex partitionless structure during rapid solidification processing has apparently revealed a unique set of kinetic conditions which may be achieved during solidification processing at high undercoolings. An analysis based on the nucleation and growth kinetics of the  $\alpha$  and  $\beta$  phases has been undertaken to define a range of undercooling levels and temperatures over which the duplex structure may develop. The steady-state, homogeneous nucleation temperatures were calculated by applying the approach taken by Thompson and Spaepen [83THO]; that is, a parallel tangent construction was used to calculate the free energy change for solidification and the Spaepen and Meyer model [76SPA] was used to calculate the solid-liquid interfacial energy. It is recognized that heterogeneous nucleation certainly must be considered for a rigorous analysis of the nucleation kinetics, so the results of the homogeneous nucleation analysis will be used to guide further modeling efforts. The calculated nucleation temperatures are shown on the metastable Ni-V diagram in figure 2b. The formation of the duplex structure could be expected to require similar nucleation temperatures for both phases. The calculated crossover of nucleation temperatures occurs at 48 at% V, which is within the range of compositions over which the duplex partitionless structure forms. Further analysis is underway to determine the range of compositions over which this duplex structure could be expected to form.

### **Mn-Al Alloy System - Ferromagnetic Metastable $\tau$ Phase**

[Refer to attachments A2 and A3]

Ferromagnetism in Mn-Al alloys was first reported by Hindricks in 1908 [08HIN] following the observation of some permeability anomalies at intermediate compositions. Later work [60KOC] has led to an improvement in the phase diagram (figure 3). The ferromagnetic properties are associated with the metastable  $\tau$  phase, which can be formed over the composition range 49-60 at% Mn. This phase is metastable with an ordered face-

centered tetragonal,  $L1_0$  structure [58KON]. In all previous work, the  $\tau$  phase has been produced only by solid state heat treatments. For example, the  $\tau$  phase may be produced from the high temperature hcp phase by cooling to temperatures below 800°C at rates between 350 and 800°C/min. At slower cooling rates the  $\tau$  phase decomposes into the equilibrium phases, while faster cooling rates result in the retention of the  $\tau$  phase. The  $\tau$  phase may also be produced by water quenching from the  $\epsilon$  phase followed by aging at temperatures between 300-700°C. When formed in the solid state, the  $\tau$  phase has a defect structure characterized by numerous antiphase boundaries, twins, and stacking faults. Thus, even though the Mn-Al alloy has a good potential for commercial permanent magnet applications, the magnetic properties have not yet been optimized due to the defects developed during the heat treatments. Both the defect structures and decomposition reactions reduce the magnetic properties. However, even with these defects the magnetic properties and low cost are attractive for some permanent magnet applications.

The ferromagnetic  $\tau$  phase is metastable but it has been produced only by solid state heat treatments, i.e. the high temperature hcp phase transforms to the metastable  $\tau$  phase. The production of  $\tau$  by solidification as a metastable product results in a reduction in the defect structure of the phase, since a single magnetic domain could form in a droplet. As a result, an enhancement of magnetic performance should be expected.

In an attempt to produce the  $\tau$  phase directly from the melt, the containerless drop tube processing technique was introduced to evaluate the Mn-Al alloy system in terms of processing variables such as melt superheat, powder particle size, and gas environment. With containerless drop tube processing, two major achievements have been established. First, the  $\tau$  phase was produced from the melt for the first time. Secondly,  $\tau$  phase was formed beyond the composition range (49-60 at% Mn) which has been claimed for over 30 years to be a requirement for the formation of  $\tau$  by conventional solid state heat treatment methods.

The Mn-Al is an excellent model system, since  $\tau$  is the only ferromagnetic phase in the system and as such  $\tau$  phase droplets may be magnetically separated on an individual particle basis. Therefore, the ferromagnetic  $\tau$  phase has allowed for product yield analysis in an accurate and statistically significant way.

Based on the current experience with Mn-Al alloys, the investigation has explored the influence of surface coating and powder size in terms of cooling rate on the level of liquid undercooling and metastable phase formation. The magnetic separation of the  $\tau$  phase was coupled with x-ray diffraction analysis to assess the relative abundance of the  $\tau$  phase product yield with the various processing parameters. With the capability of discriminating the solidification phase selection, the effects of particle size and gas environment have been assessed in this investigation.

Along with the study on the effect of particle size, the gas environment effect related to surface coating was explored in terms of gas conductivity and nucleant type for the metastable yield analysis in this investigation. Since the thermal conductivity of helium is higher than that of argon, the comparison of the metastable yield was made for the gas thermal conductivity effect.

### **Fe-Ni Alloy System - Metastable bcc Solidification**

[Refer to attachment A4]

As a further test of the application of droplet samples together with an analysis based on metastable phase diagrams and competitive kinetics, the microstructural development has been examined after solidification in undercooled Fe-Ni alloys. Even though the Fe-Ni system has been studied previously the solidification behavior has been reported in different studies to follow various pathways, with apparent dissimilarities existing as a function of sample size and processing conditions. In order to identify the possible hierarchy of microstructural pathways and transitions, a systematic evaluation of the

microstructural evolution in undercooled Fe-Ni alloys was performed on uniformly processed samples covering seven orders of magnitude in volume. At appropriate undercooling levels, alternate solidification pathways become thermodynamically possible and metastable product structures can result from the operation of competitive solidification kinetics. For thermal history evaluation, a heat flow analysis was applied and tested with large Fe-Ni alloy particles (1 to 3  $\mu\text{m}$ ), to assess undercooling potential. Alloy powders (10 to 150  $\mu\text{m}$ ), with large liquid undercoolings, were studied under the same composition and processing conditions to evaluate the solidification kinetics and microstructural evolution, including face-centered cubic (fcc)/body-centered cubic (bcc) phase selection and the thermal stability of a retained metastable bcc phase.

For the large drops (1 to 3 mm) and assuming Newtonian heat transfer conditions, *i. e.* Biot number less than  $10^{-2}$  [80LEV], and applying the Ranz-Marshall relation for a flow past a submerged sphere [60BIR], a numerical analysis of the heat flow yielded undercoolings of  $\sim 160^\circ\text{C}$  below the liquidus temperature of the fcc phase. The numerical analysis results for the alloy compositions processed in a He-2%  $\text{H}_2$  atmosphere are plotted in the upper portion of the Fe-Ni phase diagram of figure 4. From this model it is apparent that metastable bcc phase formation from the melt is thermodynamically feasible and may compete with fcc phase development.

Based upon the detailed microstructural observations there are two possible solidification pathways, as schematically shown in figure 5 either bcc or fcc phases could develop upon freezing, depending on the nucleation and growth competition. Moreover, if bcc solidification occurred, the bcc phase could decompose into the fcc and then to martensite upon cooling. During the period of recalescence and heat extraction there is sufficient time available for solid-state transformations as demonstrated by solid-state upquenching treatments. For fast cooling rates and/or sluggish kinetics decomposition the high temperature bcc phase could be retained to room temperature. It is well-known that the transition temperature  $\text{Ms}$  is relatively independent of the cooling rate [75VER] and

that martensitic phase always develops from the fcc phase. Therefore only the bcc  $\delta$  and martensite phases are possible provided that  $M_s$  is above room temperature. On the other hand the presence of an equiaxed grain structure can be explained as the result of a metastable bcc dendritic structure formed from the melt which then transformed into the stable fcc with an equiaxed grain structure before forming martensite.

In fact, the latter pathway has been confirmed by the results of upquenching treatments that are summarized in Figure 6. Essentially, the fine powders cool fast enough in the solid state to retain the metastable bcc phase solidification structure, but the large drops which cool slowly undergo a solid state reaction from the as-solidified bcc phase to an fcc phase which then transforms to martensite. Based upon this analysis a consistent, clear trend is apparent for the first time in the solidification microstructure development for Fe-Ni alloys. When the liquid undercooling falls below the metastable bcc liquidus, the bcc phase develops from the melt.

A summary of the results and analysis of solidification microstructure development in Fe-Ni alloys is presented in Figure 7. The log of droplet diameter *vs* nickel content is used as a guide to delineate regimes of microstructural development. With decreasing droplet size, larger cooling rates and undercooling apply and, combined with nucleant isolation in the solid state, can account for the change in phase retention below a certain size. The transition size was taken as the approximate droplet diameter where an equal abundance of the two different morphologies (cellular/dendritic *vs* martensitic) was found so that the trend in Figure 7 may approximate isokinetic-type behavior. Above this transition, the bcc phase formed from the melt, decomposed to the stable fcc phase, and then transformed to martensite ( $\alpha'$ ). Indeed, the transition size provides a useful means of defining and distinguishing between bulk and powder processing behavior in the Fe-Ni system. In effect, the summary plot given in figure 7 represents a map which provides in outline form the domains of microstructure development in terms of processing (i.e. sample size) and sample variables (i.e. alloy composition) that can be controlled in a

regulated manner. A more complete analysis requires a detailed consideration of the competitive reaction kinetics under the influence of a changing thermodynamic driving free energy.

### **Au-Pb-Sb System: Thermodynamic Properties and Crystallization Kinetics**

[Refer to attachment A5]

The Au-Pb-Sb system offers the potential for glass formation at a variety of cooling rates in bulk samples ranging from  $10^3$  K/s to  $10^6$  K/s [82LEE]. During cooling below the eutectic temperature, the phase selection for crystallization is determined by competition between nucleation and growth of the different metastable and stable phases. In order to predict the final transformation products which can be amorphous or crystalline, knowledge of the thermodynamic properties of the metastable liquid and solid phases in the undercooled regime becomes necessary.

The heat capacities of the undercooled liquid phase and the crystalline phase were measured in the glass-forming composition range with droplet and bulk samples. Based on the measured heat capacity data, the entropy, enthalpy, and Gibbs free energy differences between the eutectic and the undercooled liquid were determined as a function of temperature over about 60% of the undercooling range below the liquidus temperature and compared with theoretical predictions. The results indicate that an isentropy temperature of  $313 \pm 5$  K, which agrees well with the experimental data for the glass transition. The thermodynamic evaluation was applied further to develop a kinetics analysis of the nucleation response during cooling. Use of different approximations for the Gibbs free energy leads to a variation of the prefactor terms of six orders of magnitude for classical nucleation theory and, consequently, large variation in calculated transformation diagrams which is more pronounced with increasing undercooling. Extrapolations into the glass-forming temperature range and the effects of viscosity, transient nucleation, and

estimated Kauzmann temperatures on the crystallization kinetics at high undercooling have been evaluated. This analysis reveals the importance of using measured values of thermophysical properties, even if they represent a limited temperature range at modest undercooling, rather than model approximations in order to obtain reliable evaluations of crystallization kinetics at high undercooling in the glass-forming range.

### **Analysis and Modeling of Sample Thermal History and Solidification Kinetics**

The availability of thermal history information, such as the level of undercooling, is central to the proper interpretation of a solidification microstructure. To determine the thermal history of a droplet in containerless drop tube processing, direct thermal measurement of a falling droplet was conducted using a calorimetric method. With a given level of superheat, the heat content of a droplet has been determined at the time of impact with the calorimeter by means of a simple heat balance. The proposed thermal measurements using a calorimetric system have not only allowed for the complete thermal history of the falling droplet, but have also allowed for some insight on the solidification kinetics. The method has been successfully implemented with pure tin droplets and will be used to analyze alloy droplets in future work.

Experimental results in the metastable yield analysis of powders have defined three critical parameters in the alteration of solidification pathway development: melt superheat, processing environment, and particle size. By using particle size as a reference, the relative effect of other process parameters can be calculated and experimentally verified. In particular, the relative effect of the processing environment on metastable yields can be isolated to three factors: nucleant type, gas conductivity, and nucleant density. Statistical analysis of metastable yield in the droplet population as a function of processing conditions will provide a basis for greater control of solidification structure. These results will then be considered in the nucleation and growth kinetics analysis for metastable phase formation.

As a further aid to solidification analysis, droplet microstructure were used as a guide to understand sample thermal history. The relationship between microstructural scale and level of undercooling achieved illustrates the importance of microstructure as an *in situ* probe for quantitative evaluation of material properties. The relationship between eutectic spacing and level of undercooling illustrates this point. Modeling of eutectic solidification in the InSb-Sb system could be validated by comparing the calculated undercooling with the experimental value. Microstructural analysis may also be used to assess the effect of heat flow on growth behavior. A transition of eutectic morphology develops in InSb-Sb alloys as a result of a change in heat flow conditions. A rod-type structure initially develops following nucleation. With increasing fraction solid, the rod spacing increases, implying a decrease in solidification rate. A transition to a lamellar morphology occurs due to a change in the dominant heat flow mechanism. Initially, heat flow to the undercooled liquid ahead of the interface dominates, but with increasing fraction solid, a transition to a lamellar morphology develops as a result of external heat flow. This example illustrates the importance of heat flow modeling combined with microstructural analysis to provide an understanding of droplet solidification. The concept of an *in situ* probe has particular significance to containerless processing in space in that the effect of disturbances such as external positioning fields on solidification behavior may be analyzed in a systematic way. The experimental determination of undercooling level through non-contact temperature measurement in the investigation has provided a test of the solidification and heat flow models which were developed in order to provide insight into the mechanisms of solidification microstructure development and to the design of the science requirements for a space experiment.

## Summary

The microgravity environment provides new opportunities for the control of solidification processes, and the containerless environment afforded by microgravity conditions avoids

crucible-induced sample contamination and allows for large undercooling. By analyzing key containerless processing parameters in a ground based drop tube study, a carefully designed space flight experiment may be planned.

The investigation has focused on the control of microstructural evolution in Mn-Al, Ni-V, Fe-Ni, and Au-Pb-Sb alloys through the high undercooling levels provided by containerless processing, and the study has provided fundamental new information on the control of nucleation. Solidification analysis has been conducted by means of thermal analysis, x-ray diffraction, and metallographic characterization. This investigation has contributed to the understanding of terrestrial solidification processing and has demonstrated that microgravity materials processing can yield novel microstructures and phases that have not been observed previously with terrestrial processing approaches.

The Mn-Al alloy system offers a useful model system with the capability of phase separation on an individual particle basis, thus permitting a more complete understanding of the operative kinetics and the key containerless processing variables. This system has provided the opportunity of analyzing the nucleation rate as a function of processing conditions and has allowed for the quantitative assessment of the relevant processing parameters. These factors are essential in the development of a containerless processing model which has a predictive capability. Similarly, Ni-V is a model system that has been used to study duplex partitionless solidification, which is a novel structure possible only in high undercooling solidification processes. Nucleation kinetics for the competing bcc and fcc phases were studied to determine how this structure can develop and the conditions under which it may occur.

As a further test of the application of droplet samples together with an analysis based on metastable phase diagrams and competitive kinetics, the microstructural development has been examined after solidification in undercooled Fe-Ni alloys. In order to identify the possible hierarchy of microstructural pathways and transitions, a systematic evaluation of the microstructural evolution in undercooled Fe-Ni alloys was performed on

uniformly processed samples covering seven orders of magnitude in volume. A map of the domains of microstructure development was developed in terms of processing (i.e. sample size) and sample variables (i.e. alloy composition) that can be controlled in a regulated and systematic manner.

The Au-Pb-Sb system has been investigated to provide a comparison between measured thermophysical properties and values calculated from model approximations. The heat capacities of the relevant phases as well as values of thermodynamic functions were experimentally evaluated over a range of temperatures. The thermodynamic data was used to develop a kinetics analysis of the nucleation behavior at various undercoolings. The glass transition was also investigated with thermodynamic and kinetic models.

**Attachments**

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Parameter	Undercooling Response	Remarks
Droplet Size	Increased $\Delta T$ with size refinement at constant $\dot{T}$	Nucleant isolation follows Poisson statistics
Droplet Coating	Function of coating structure and chemistry; major effect in limiting $\Delta T$	Most effective coating is catalytically inert
Cooling Rate	$\Delta T$ generally increases with increasing $\dot{T}$	Changing $T$ can alter nucleation kinetics
Melt Superheat	System Specific	Likely related to coating catalysis
Composition	$T_n$ follows trend of $T_L$	Melt purity not usually critical
Pressure	$T_n$ parallels melting curve trend	Change in response can signal formation of alternative phase

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Figure 1: Effect of processing parameters on undercooling

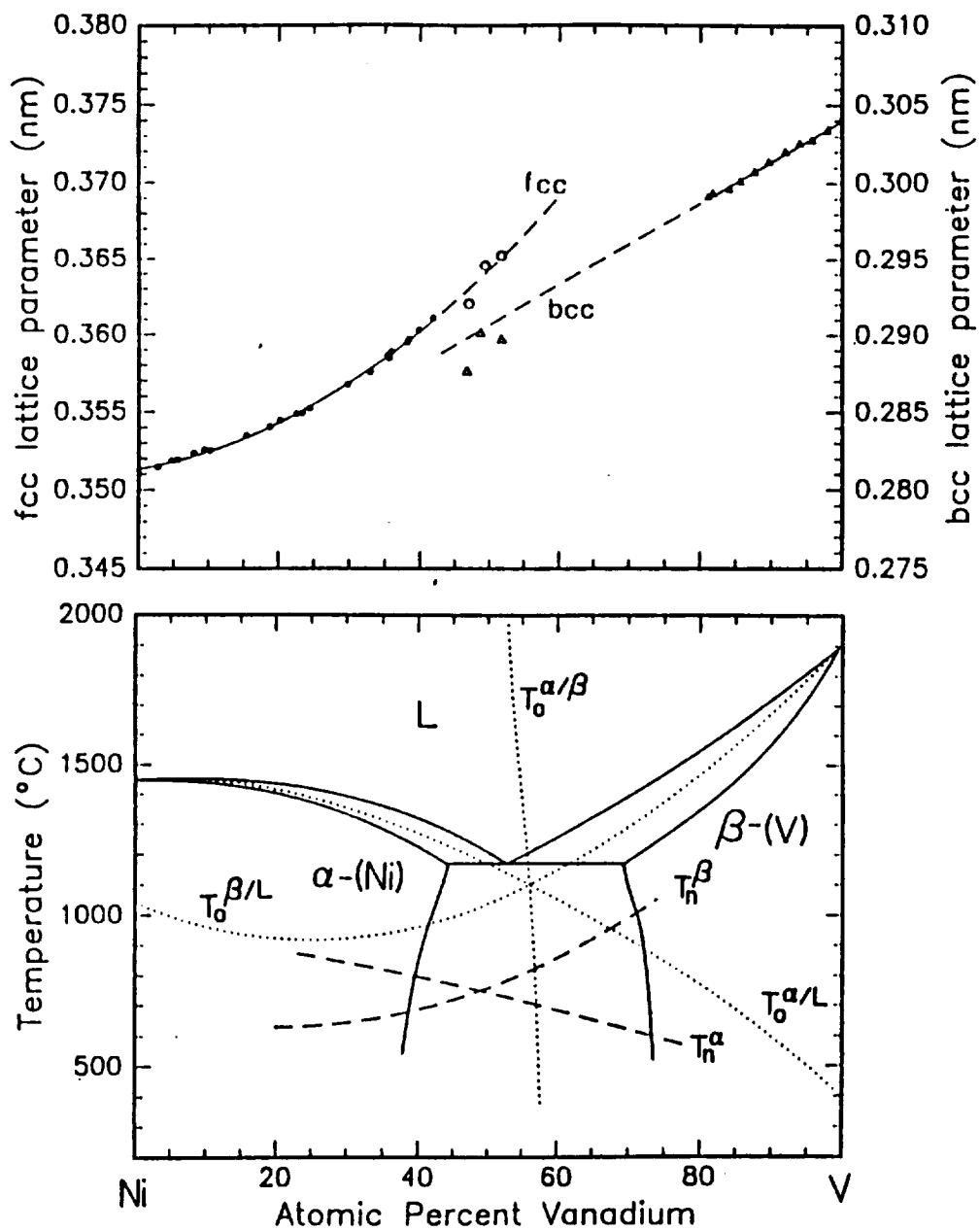


Figure 2: Top: lattice parameter curves for the  $\alpha$  and  $\beta$ . Solid symbols - equilibrium data; open symbols - this study. Bottom: Ni-V metastable phase diagram with calculated  $T_n$  and  $T_0$  curves.

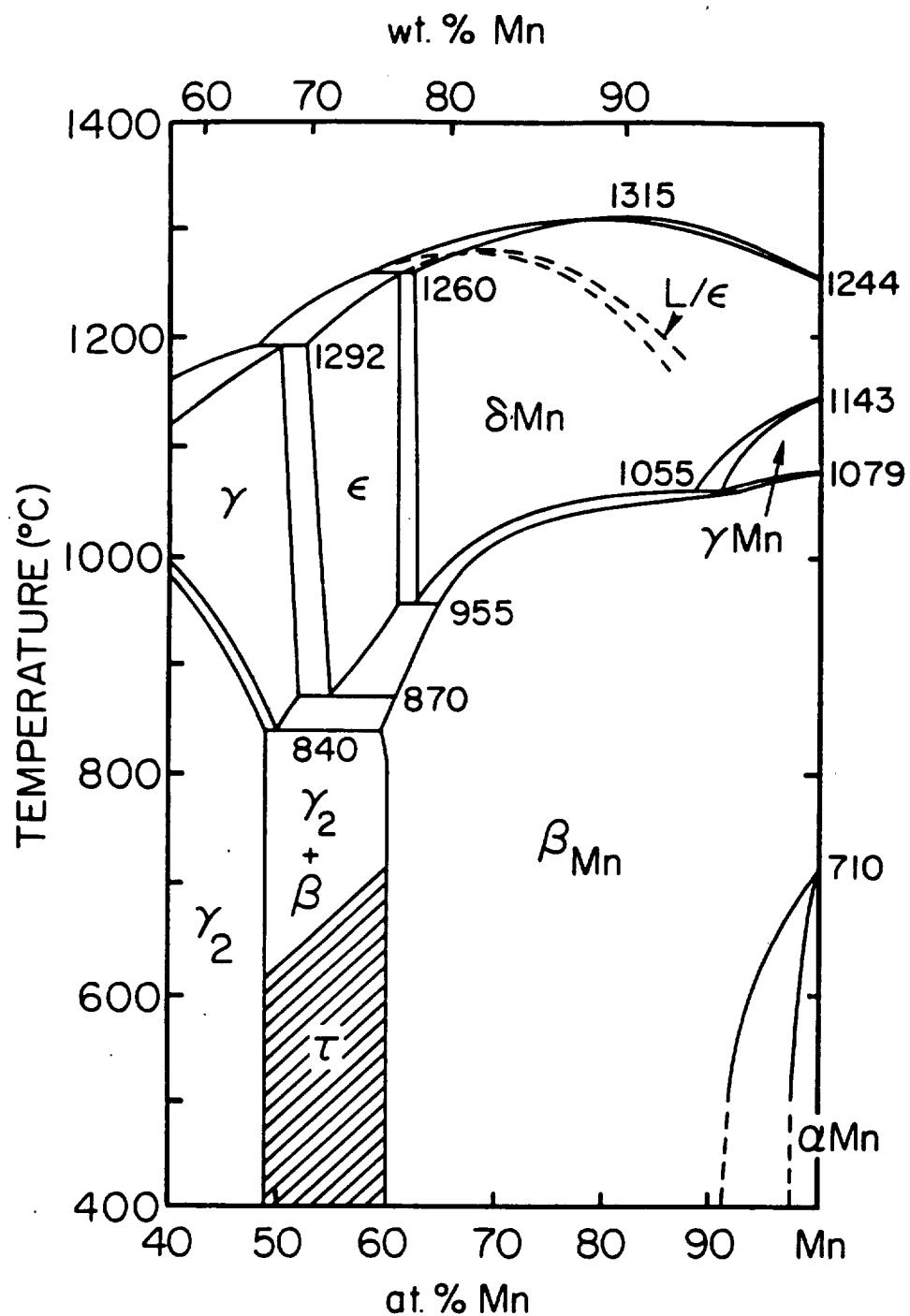


Figure 3: Mn-Al equilibrium phase diagram.

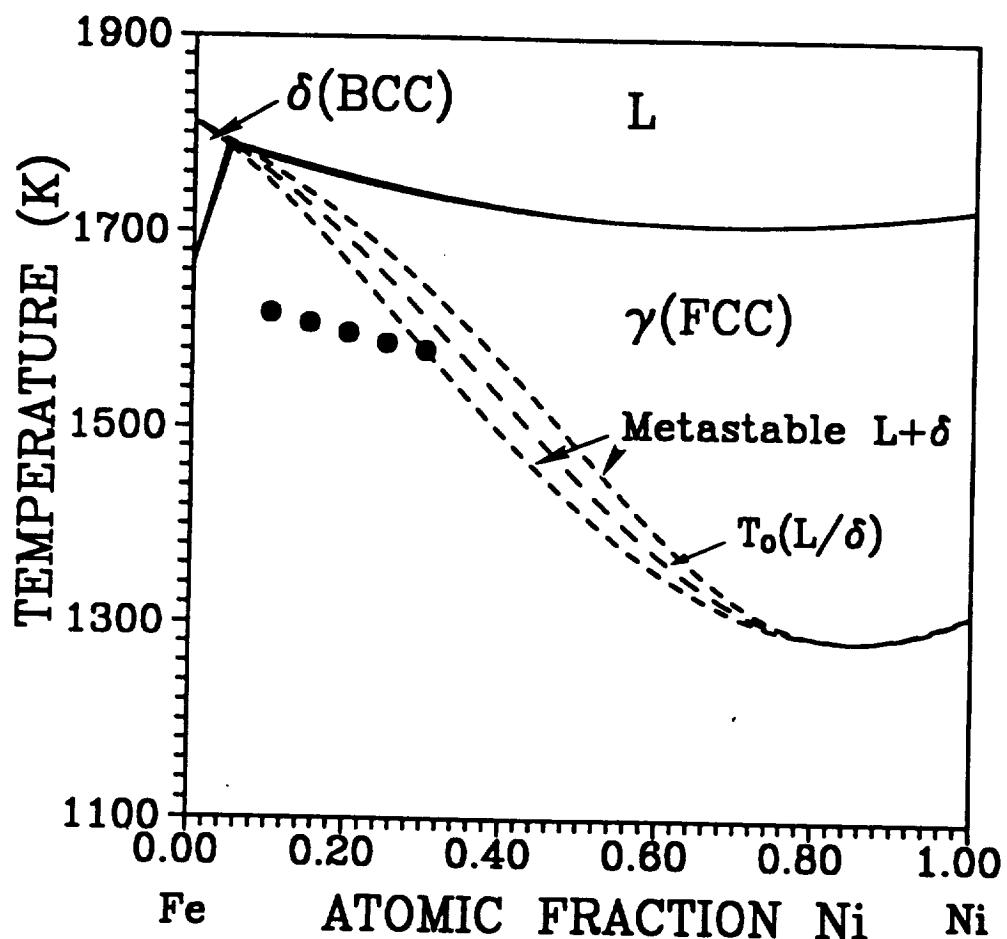


Figure 4: High-temperature Fe-Ni phase diagram based on assessed data and a model calculation with the metastable phase equilibria indicated by dashed lines. Undercooling levels of the large droplets processed in He-2% H<sub>2</sub> are denoted by closed circles.

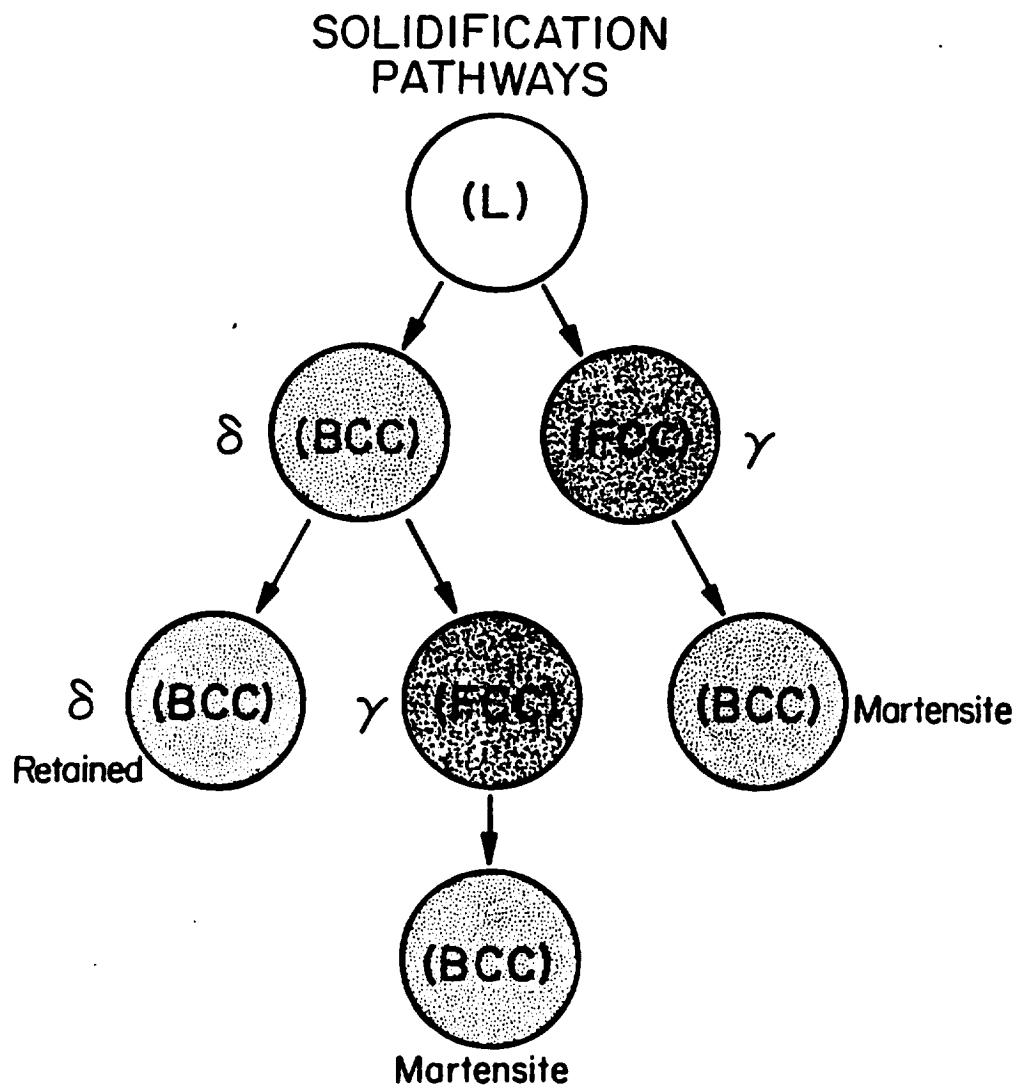


Figure 5: Schematic of two possible solidification pathways and different solid state reactions for drop-tube processed samples.

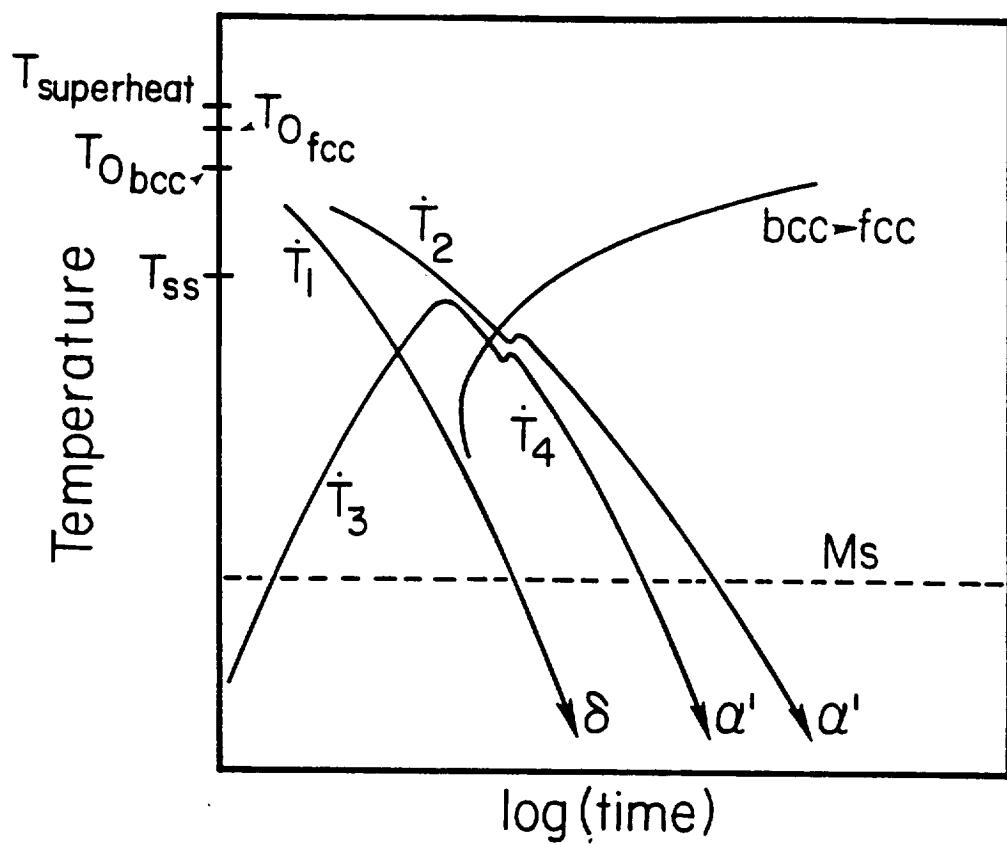


Figure 6: Schematic of solid-state powder processing pathways in Fe-15 wt% Ni superimposed on a continuous cooling transition curve for bcc  $\rightarrow$  fcc:  $\dot{T}_1$  = cooling of solid powder ( $d = 30$  to  $44 \mu\text{m}$ ) processed from the melt;  $\dot{T}_2$  = cooling of solid powder ( $75$  to  $100 \mu\text{m}$ );  $\dot{T}_3$  = heating of solid powder ( $30$  to  $44 \mu\text{m}$ ) during reprocessing in the solid state; and  $\dot{T}_4$  = cooling of solid powder ( $30$  to  $44 \mu\text{m}$ ) during reprocessing in the solid state.

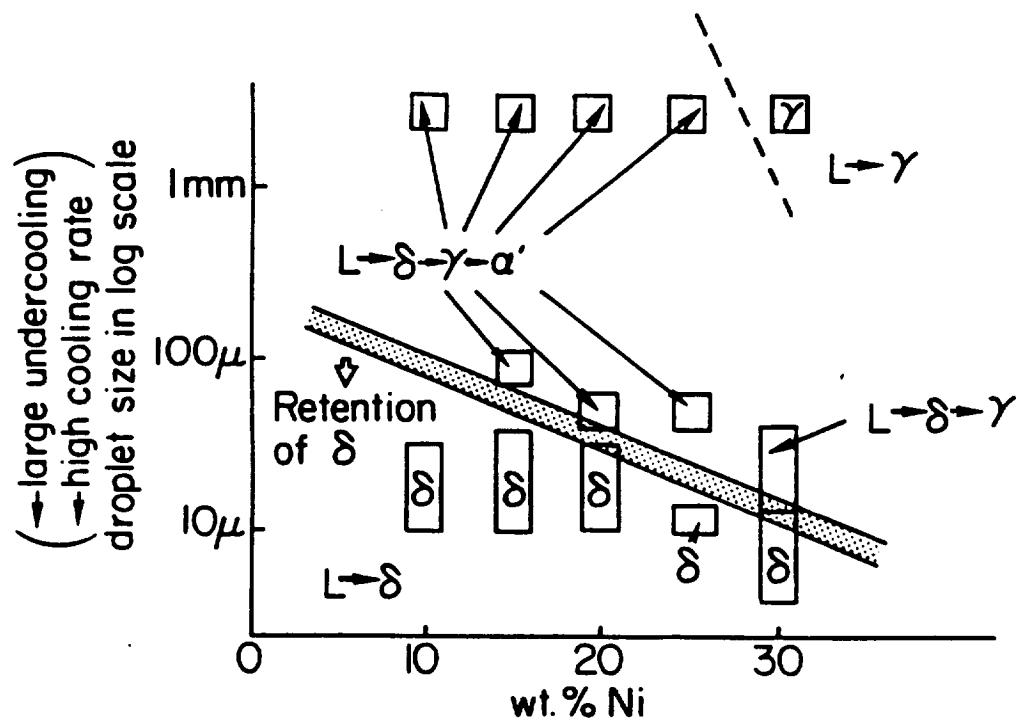


Figure 7: Summary of the structural evolution in the drop tube processing of Fe-Ni alloy in a He-2% H<sub>2</sub> environment.